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# Evaporation of a Collection of Liquid Drops

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# EVAPORATION OF A COLLECTION OF LIQUID DROPS

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## I. Introduction and Summary.

In a collection of evaporating drops, such as an aerosol, each drop is affected by the presence of the other drops. The evaporation of these other drops tends to raise the vapor pressure or concentration in the neighborhood of any drop above what it would be if that one drop evaporated alone. In effect, the drops compete for space into which to evaporate. If there are N drops per unit volume of aerosol then each drop has an effective volume of $N^{-1}$ into which to evaporate. Therefore we take, as a model of a collection of evaporating drops, a single drop within an impermeable container of volume $N^{-1}$. For mathematical convenience we assume that the container is a sphere with the drop - also a sphere - at its center. Then we have to determine the radius $R(t)$ of the drop as a function of time. To do so we must simultaneously consider the concentration $c(r, t)$ in the space between the drop and the container, the radius of which we call M.

The physical principles on which this determination is based are:

a) The flow of vapor is assumed to satisfy Fick's law and therefore the concentration satisfies the diffusion equation.

b) The concentration is assumed to have a constant value - the saturation value - at the drop surface.

c) The rate at which the drop radius decreases is assumed to be proportional to the rate at which vapor diffuses away from the drop surface, (i.e. conservation of matter).

d) No vapor flows through the container.

e) The concentration is assumed to be initially uniform throughout the space between the drop and the container.

f) Temperature changes and heat flow are ignored - the process is assumed to be isothermal.

Mathematically these conditions, from which $R(t)$ and $c(r,t)$ can be determined, are, as given in [6]

$$(1) \qquad c_{rr} + \frac{2}{r} c_r = c_t \qquad \text{for } M > r > \max[0, R(t)], \quad t > 0$$

$$(2) \qquad c[R(t), t] = 1 \qquad \text{for} \qquad 0 \leq t \leq t_0$$

$$(3) \qquad \alpha c_r[R(t), t] = \dot{R}(t) \qquad \text{for} \qquad 0 < t < t_0$$

$$(4) \qquad c(r, 0) = 0 \qquad \text{for} \qquad 1 < r < M$$

$$(5) \qquad c_r(M, t) = 0 \qquad \text{for} \qquad t \geq 0$$

$$(6) \qquad R(0) = 1$$

$$(7) \qquad c_r(0, t) = 0 \qquad \text{for} \qquad t > t_0$$

In equations (1) - (7) all quantities are in the dimensionless form given in [3] (see eqs. (7) - (12) of [3]). Therefore since the initial drop radius is the unit of length and the container radius must exceed the drop radius, we have the restriction $M \geq 1$. The constant $t_0$ is the time required for complete evaporation, if it occurs, and is infinite if complete evaporation does not occur. The constant $\alpha$ is a given positive number determined by the coefficient of diffusion, the density of the liquid in the drop, the initial concentration, the saturation concentra-

tion and the initial drop radius.

The problem formulated above reduces, when $M = \infty$, to the case of a drop in infinite space with no container, which was treated in [3] and [5]. In [3] approximate results were obtained for $R(t)$ and for $t_0$ by formal calculation. In [5] it was proved that the problem with $M = \infty$ has a unique solution and that the drop completely evaporates in a finite time. A process for constructing the solution was presented and upper and lower bounds for $R(t)$ and for $t_0$ were obtained which agree closely with the approximate results of [3]. For practical applications the upper and lower bounds are so close together that they determine $R(t)$ and $t_0$ with satisfactory accuracy.

In the present case in which the drop is enclosed within a container of finite radius M the problem formulated above also has a unique solution for $R(t)$ and $c(r, t)$. The radius $R(t)$ is a monotonically decreasing function of t but the drop does not always evaporate completely. Whether or not this happens depends upon the container radius M. There is a critical value of the container radius $\overline{M} = (\alpha^{-1} + 1)^{1/3}$ such that for $M > \overline{M}$ the drop does evaporate completely in a finite time and the concentration everywhere within the container approaches the constant value $c_\infty = (\overline{M}/M)^3$ as $t \longrightarrow \infty$. When $M = \overline{M}$ the drop radius $R(t)$ approaches zero as $t \longrightarrow \infty$, and the concentration approaches unity. If $M < \overline{M}$ the drop does not evaporate completely, but instead its radius approaches the value $[1 - \alpha(M^3 - 1)]^{1/3}$ and the concentration approaches unity as $t \longrightarrow \infty$. All of these results, which are quite reasonable and almost obvious physically, have been proved and are reported on in this report. However the existence of the solution

is proved only when $\alpha$ or $M$ satisfy certain conditions. Undoubtedly the solution exists for all $\alpha \geq 0$ and all $M \geq 1$, but other methods are necessary to prove it.

In addition to the proofs of the above statements, the main results of the present report pertain to the determination of the radius-time curve $R(t)$ and the evaporation time $t_o$. It is shown that the function $R(t)$ is the limit of the sequence of functions $\rho_m(t)$ constructed in section IV. More useful than this fact, however, is the result that the functions $\rho_m(t)$ also provide upper and lower bounds for $R(t)$ and for the rate of evaporation $\dot{R}(t)$. Explicitly this result is that for any value of n

$$(8) \qquad \rho_{2n}(t) \leq R(t) \leq \rho_{2n+1}(t)$$

$$(9) \qquad \dot{\rho}_{2n}(t) \leq \dot{R}(t) \leq \dot{\rho}_{2n+1}(t) \quad .$$

By means of these equations arbitrarily close bounds on $R$ and $\dot{R}$ can be obtained. These results have only been proved for restricted values of $\alpha$ or of $M$ - for other values of these constants they have been proved for only a limited period of time. As an example of the use of these results the following lower bound on $R(t)$ has been obtained using only the first term in the sequence $\rho_0(t)$. The bound, which holds if $M > 3$, is

$$(10) \qquad R^2(t) \geq 1 + \frac{4\alpha M}{\sqrt{\pi}} \left[\sqrt{t} + \frac{M^2-2M-1}{\sqrt{\pi}(M-1)} \log\left(1 - \frac{\sqrt{\pi}(M-1)}{M(M-3)}\sqrt{t}\right)\right]$$

A similarly obtained lower bound on $\dot{R}(t)$ is given in equation (68).

Other bounds on $R(t)$ and on $t_o$, when $t_o$ is finite, are given in the following theorem, which is proved by means of Green's

theorem in section VI.

(11) Theorem 8.

a) $R^2(t) \leq 1 - \frac{2\alpha t}{1+\alpha}(1 - c_\infty) \equiv \phi(t)$

b) $R^2(t) \geq 1 - \alpha(M^2-1) - 2\alpha t \equiv \chi(t)$

c) $R^2(t) \leq \dfrac{3M\phi(t)-2}{3M-2\sqrt{\phi(t)}} \equiv \Psi(t)$ for $\phi(t) \geq 0$

d) $R^3(t) \geq 1 - \alpha(M^3-1) \equiv R^3_\infty$, for $M \leq \bar{M}$

e) $t_o \geq \frac{1}{2\alpha} - \frac{1}{2}(M^2 - 1)$, for $M > \bar{M}$

f) $t_o \leq \frac{\alpha+1}{2\alpha}\left(\frac{1-2/3M}{1 - c_\infty}\right)$, for $M > \bar{M}$

The expression $R_\infty$ occurring in the lower bound in (d) is the exact final radius for the case $M \leq \bar{M}$, while the upper bounds in (a) and (c) reduce, in this case to the trivial bound $R \leq 1$. For $M > \bar{M}$, $R(t)$ vanishes at a finite time $t_o$ and then all bounds except (d) yield significant information.

In Figures 1, 2, and 3 the applicable bounds on $R(t)$ are shown for the cases $M = 20$, $60$ and $200$ respectively, i.e. container radius = 20, 60 or 200 initial drop radii. The constant $\alpha$ has been chosen as $\alpha = 2 \times 10^{-5}$, corresponding to the evaporation of a drop of water in air. For this choice of $\alpha$, $\bar{M} = 36.84$, so that in the case $M = 20 < \bar{M}$ the drop does not evaporate completely.

In this case (Fig. 1.) the drop radius is bounded from below by the constant $R_\infty$. We also have the lower bounds $\psi(t)$ (good initially) and $\chi(t)$ ( a transition bound). The upper bound $\phi \equiv 1$ merely states that the drop evaporates while $P(t)$ is a fair

bound during its short period of applicability.

In Fig. 2, for $M = 60 > \overline{M}$, the drop evaporates in finite time ($2.32 \times 10^4 \leq t_0 \leq 3.22 \times 10^4$) and again Theorem 7 supplies rough bounds over the full range, while the iteration gives $\psi(t)$ an excellent lower bound initially but applicable for only a short time. The curve $\chi(t)$, (included for comparison), represents the actual solution for $M = \infty$ since the upper and lower bounds for this case, (see [5], p. 2) coincide within the accuracy of this graph.

For M = 200, Fig. 3, the upper bound $\phi(t)$ coincides (within graphical accuracy with $\chi(t)$ while now it is the lower bound $\psi(t)$ which yields a better result than $\chi(t)$.

It seems likely that much better bounds can be obtained than those given here, and therefore the most important results of this report are the methods and not the actual bounds. In fact, the same methods have been applied to the corresponding one dimensional problem(evaporation of a slab in a bounded region) and the bounds obtained were excellent. It is to be hoped that similar results will be obtained in the present problem as well.

## II. Reformulation of the Problem.

Instead of c(r, t) it is more convenient to deal with the function u(r, t) defined by

$$u(r, t) = rc(r, t) . \tag{12}$$

From (1)-(7) we obtain the following equivalent set of equations for u(r, t) and R(t)

(13) $u_{rr} = u_t \quad , \qquad \text{for} \quad n > r > \max[0, R(t) \ , \quad t > 0$

(14) $u(R(t),t) = R(t) \ , \qquad \text{for} \quad 0 \leq t \leq t \ .$

(15) $\alpha u_r(R(t),t) = R(t)\dot{R}(t) + \alpha \ , \quad \text{for} \quad 0 < t < t_o$

(16) $u(r, 0) = 0 \quad , \qquad \text{for} \quad 1 < r < M$

(17) $Mu_r(M, t) - u(M, t) = 0 \qquad \text{for} \quad 0 \leq t$

(18) $R(0) = 1$

(19) $\lim\limits_{r \to 0} \frac{u}{r}$ exists and is bounded for $t > t_o$

(20) $\lim \dfrac{ru_r - u}{r^2} = 0 \ , \qquad t > t_o \quad .$

In the range $0 \leq t \leq t_o$ the conditions (19) and (20) can be disregarded. We now seek two functions $u(r, t)$ and $R(t)$ which satisfy (13)-(20).

## III. Method of Solution

The problem formulated in (13-18) is a free boundary value problem for the heat equation. To solve it we follow the general method for solving such problems given in [4].

The first step in this method is to construct an auxiliary function $u^\rho(r, t)$ which we now proceed to define. Let $\rho(t)$ be a smooth function such that $\rho(0) = 1$. We use the notation

$$u^\rho(\rho^{\pm}, t) = \lim_{0<\varepsilon \to 0} u^\rho(\rho(t) \pm \varepsilon, t)$$

$$u_r^\rho(\rho^{\pm}, t) = \lim_{0<\varepsilon \to 0} u_r^\rho(\rho(t) \pm \varepsilon, t)$$

The function $u^\rho(r, t)$ is then defined for $-\infty < r < M$, $r \neq \rho(t)$, $t > 0$ by the following conditions:

$$(21) \qquad u^\rho_{rr} = u^\rho_t \qquad r \neq \rho(t), \quad -\infty < r < M$$

$$(22) \qquad u^\rho(\rho^+, t) - u^\rho(\rho^-, t) = \rho(t)$$

$$(23) \qquad a[u^\rho_r(\rho^+, t) - u^\rho_r(\rho^-, t)] = \rho(t)\dot{\rho}(t) + a$$

$$(24) \qquad u^\rho(r, 0) = 0 \;, \quad r < M \;; \quad \lim_{r \to -\infty} u^\rho(r, t) = 0$$

$$(25) \qquad Mu^\rho_r(M, t) - u^\rho(M, t) = 0 \;, \quad t > 0 \;.$$

To find $u^\rho$, we write it as a sum $v^\rho + w^\rho$, where $v^\rho$ is defined for $-\infty < r < \infty$ and satisfies equations (21) to (24), while $w^\rho$ is a compensating part defined for $r < M$ in such a way that the sum also satisfies the condition (25). The unique solution for $v^\rho$ has been found in [5], page 7, equation (19). As to $w^\rho$, we try to represent it in the form

$$(26) \qquad w^\rho(r, t) = - \int_0^t [M\, v^\rho_r(M, \sigma) - v(M, \sigma)]a(r, t - \sigma)d\sigma \cdot$$

Here $a(r, t - \sigma)$ is to be determined in such a way that $w^\rho$ satisfies (21) and (24) while $v^\rho + w^\rho$ is to satisfy (25). We then get the requirements $a_{rr} = a_t$, and $a(r, 0) = 0$ to satisfy the former condition, while to satisfy the latter, $Ma_r(r, t - \sigma) - a(r, t - \sigma)$ must be a "delta function". Since $(Ma_r - a)$ also satisfies the heat equation, we now find, by using the well known properties of the fundamental solution of the heat equation, see [1], that

$$(27) \qquad Ma_r(r,\ t - \sigma) - a(r,\ t - \sigma) = -\frac{1}{2}\,\frac{r-M}{(t-\sigma)^{3/2}}\,\eta\left(\frac{r-M}{2\sqrt{t-\sigma}}\right)$$

where

$$(28) \qquad \eta(x) = \pi^{-1/2} \exp(-x^2) .$$

Solving (27) for a, we get, on using the condition $a \to 0$ as $|r| \to \infty$ ,

$$a(r,\ t - \sigma) = \frac{2}{M^2} \exp\left(\frac{t-\sigma}{M^2} + \frac{r-M}{M}\right) \int_{-\infty}^{\frac{r-M}{2\sqrt{t-\sigma}} + \frac{\sqrt{t-\sigma}}{M}} \eta(\sigma)\,d\sigma$$

$$+ \frac{1}{M\sqrt{t-\sigma}}\,\eta\left(\frac{r-M}{2\sqrt{t-\sigma}}\right) .$$

Inserting this in (26) and adding it to $v^\rho$ we now get, after some simplifications,

$$(29) \quad u^\rho(r,\ t) = r\left[\int_{z(r,0)}^{z(r,t)} \eta(\sigma)\,d\sigma + \int_{\zeta(r,0)}^{\infty} \eta(\sigma)\,d\sigma\right] - \sqrt{t}\,\Big[\eta(z(r,0)) - n(\zeta(r,0))\Big]$$

$$- \frac{1}{2a}\int_0^t \frac{\rho(\sigma)\dot{\rho}(\sigma)}{\sqrt{t-\tau}}\,[\eta(z) + \eta(\zeta)]\,d\sigma$$

$$- 2(M-1)\exp\left(\frac{t}{M^2} - \frac{2\sqrt{t}\,\zeta(r,0)}{M}\right)\int_{-\frac{\sqrt{t}}{M} + \zeta(r,0)}^{\infty} n(\sigma)\,d\sigma$$

$$- \frac{2}{aM}\int_0^t \rho(\sigma)\dot{\rho}(\sigma)\exp\left(\frac{t-\sigma}{M^2} - \frac{2\sqrt{t-\sigma}}{M}\,\zeta\right)\left(\int_{-\frac{\sqrt{t-\sigma}}{M} + \zeta}^{\infty} \eta(\tau)\,d\tau\right)d\sigma .$$

Here

$$(30)\quad \begin{cases} z = z(r,\sigma) = \dfrac{r-\rho(\sigma)}{2\sqrt{t-\sigma}} & z(r,0) = \dfrac{r-1}{2\sqrt{t}} \\[2ex] \zeta = \zeta(r,\sigma) = \dfrac{2M-r-\rho(\sigma)}{2\sqrt{t-\sigma}} ; & \zeta(r,0) = \dfrac{2M-r-1}{2\sqrt{t}} \\[2ex] z(r,t) = \begin{matrix} +\infty & \text{if} & r > \rho(t) \\ 0 & \text{if} & r = \rho(t) \\ -\infty & \text{if} & r < \rho(t) \end{matrix} & \end{cases}$$

It is observed that the formula (29) for $u^{\rho}$ is defined for $r = \rho(t)$, and we shall say that $u^{\rho}(r,t)$ takes on this value for $r = \rho(t)$. Differentiating (29) we get

$$\begin{aligned}(31)\quad u^{\rho}_{r}(r,t) = & \int_{z(r,0)}^{z(r,t)} \eta(\sigma)d\sigma + \int_{\zeta(r,0)}^{\infty} \eta(\sigma)d\sigma - \frac{1}{2\sqrt{t}}\Big[\eta(z(r,0)) - \eta(\zeta(r,0)\Big] \\ & + \frac{1}{2a}\int_{0}^{t} \frac{\rho(\sigma)\dot{\rho}(\sigma)}{t-\sigma}\Big\{z\eta(z) - \Big(\frac{2\sqrt{t-\sigma}}{M} + \zeta\Big)\eta(\zeta)\Big\}d\sigma \\ & - \frac{2(M-1)}{M}\exp\Big(\frac{t}{M^2} - \frac{2\sqrt{t}\zeta(r,0)}{M}\Big)\int_{-\frac{\sqrt{t}}{M}+\zeta(r,0)}^{\infty} \eta(\sigma)d\sigma \\ & - \frac{2}{aM^2}\int_{0}^{t} \rho(\sigma)\dot{\rho}(\sigma)\exp\Big(\frac{t-\sigma}{M^2} - \frac{2\sqrt{t-\sigma}}{M}\zeta\Big)\Big(\int_{-\frac{\sqrt{t-\sigma}}{M}+\zeta}^{\infty}\eta(\tau)d\tau\Big)d\sigma .\end{aligned}$$

Formula (31) for $u^{\rho}_{r}$ has, likewise, a meaning when $r = \rho(t)$, and we shall say $u^{\rho}_{r}$ takes on this value when $r = \rho(t)$ .

Concerning the function $u^{\rho}$ we now state the following

Theorem 1

a) $u^{\rho}$, $u^{\rho}_{r}$ are continuous for $r < \rho(t)$, and $\rho(t) < r < M$, $t > 0$

b) $u^{\rho}$ is the unique solution of problem (21) through (25) .

c) While $u^\rho$ and $u_r^\rho$ are discontinuous for $r = \rho(t)$, we have,

$$u^\rho(\rho^\pm, t) = u^\rho(\rho, t) \pm \tfrac{1}{2}(t)$$

$$u_r^\rho(\rho^\pm, t) = u_r^\rho(\rho, t) \pm \tfrac{1}{2}(\alpha^{-1}\rho(t)\dot{\rho}(t) + 1) .$$

This theorem, as well as other theorems not proved here, are proved in [10] .

The remaining theorems assert that $u^R$ with $\rho$ replaced by an appropriate $R(t)$ represents the solution to the original problem. $R(t)$ is the evaporation curve. It is defined as the solution of the equation

$$(32) \qquad Mu_r^\rho(\rho^-, t) - u^\rho(\rho^-, t) = 0 , \quad \rho(0) = 1$$

Theorem 2

Equation (32) has a unique solution $R(t)$ at least in the interval $0 \leq t \leq \min(t_o, T)$ where $t_o$ is such that $R(t_o) = 0$ and $T$ is defined in Section IV by equation (55). In this range $R(t)$ is continuous, while it is differentiable in the open interval, and is monotonically decreasing; near $t = 0$, $\dot{R}(t) = O(t^{-1/2})$ .

Theorem 3.

$$u^R(r, t) \equiv 0 \quad \text{for } r < R(t), \quad 0 \leq t \leq \min(t_o, T) .$$

Theorem 4.

$$u(r, t) = u^R(r, t) \quad \text{for } R(t) < r \leq M , \quad 0 \leq t \leq \min(t_o, T)$$

satisfies equations (13) through (18) and hence, with R(t) determined by equation (32) constitutes the unique solution of the problem in the indicated range.

It will be shown later that both possibilities $t_o > T$ and $t_o < T$ can arise, depending on the value of M. Thus for that range of M for which $t_o < T$ we have obtained the complete solution, since we can extend u for $t > t_o$ by the same process as that used in [5]. When $t_o > T$ we have obtained an incomplete solution of the mathematical problem although the results may still be sufficient for any practical applications.

In proving Theorems 1 - 4 we find that Theorem 1 is almost a direct consequence of a corresponding theorem in [5] although certain modifications are necessary. It is in attempting to prove Theorem 2 by the iteration method that we are forced to restrict the time interval (see Sec. IV-2). Theorem 3 requires an entirely different proof from that used for the corresponding theorem in [5]. It is necessary to apply the Strong Maximum Principle of Nirenberg [8] and also a theorem suggested by Nirenberg concerning the normal derivatives of solutions of parabolic equations near a maximum point which occurs on the boundary. The theorem is analogous to that of Hopf [2] for elliptic equations.

The proof of Theorem 4 follows the lines of the corresponding proof in [5] .

## IV. The Equation for R(t) and its Solution

The equation for the evaporation curve, that is equation (32), involves certain limits which can be evaluated by using Theorom lc. We then get instead of (32),

$$(32') \qquad M\left(u_r^{\rho}(\rho,t) - \frac{1}{2\alpha}\,\rho\dot{\rho} - \frac{1}{2}\right) - \left(u^{\rho}(\rho,\, t) - \frac{1}{2}\rho\right) = 0, \quad \rho(0) = 1$$

This may be rewritten in the following form

$$(33) \qquad \rho\dot{\rho} = V[\rho] \equiv 2\alpha\left\{ u_r^{\rho}(\rho,\, t) - \frac{1}{M}\, u^{\rho}(\rho,\, t) - \frac{1}{2} + \frac{1}{2M}\rho \right\}, \ \rho(0) = 1$$

The functional $V[\rho]$, is explicitly, on using (29) and (31),

$$(34) \qquad V[\rho] = 2\alpha\left(1 - \frac{\rho(t)}{M}\right)\left[\int_{z(\rho,0)}^{-\infty} \eta(\sigma)d\sigma + \int_{\zeta(\rho,0)}^{\infty} \eta(\sigma)d\sigma\right]$$

$$- \alpha\left(\frac{1}{\sqrt{t}} - \frac{2\sqrt{t}}{M}\right)\left[\eta(z(\rho,\, 0) - \eta(\zeta(\rho,0))\right]$$

$$+ \int_0^t \frac{\rho(\sigma)\dot{\rho}(\sigma)}{t-\sigma}\left\{\left(z + \frac{\sqrt{t-\sigma}}{M}\right)\eta(z) - \left(\zeta + \frac{\sqrt{t-\sigma}}{M}\right)\eta(\zeta)\right\} d\sigma.$$

At this point it is possible to explain why equation (32) was chosen for the determination of R(t) while according to the general theory of [4] other equivalent equations, apparently simpler, could have been used, and while in the case of the unconfined drop discussed in [5] the equation $u_r^{\rho}(\rho^-,\, t) = 0$ was used successfully (see equation (22) there). If one would follow the routine of [5], the equation for R(t) would be much more complicated, since all the

exponential factors appearing in equation (31) would be reflected in it. It is only by using combinations of terms appearing in (32) that one manages to get rid of a number of unwieldy exponential terms.

In solving (33) we are guided, to some extent, by the techniques used in [5]. In [5], Kolodner produces an alternating sequence of functions, which converges to the solution R(t), by exploiting the fact that the operator appearing in his equation is a "decreasing functional". His method has been extended (see [7]) to include operators which can be written as the sum of a "decreasing" and an "increasing" functional. In our case, for the operator $V[\rho]$ in (34) we can write

$$(35) \qquad V[\rho] = D[\rho] + I[\rho]$$

where

$$(36) \quad D[\rho] = -2a\left[\int_{-z(\rho,0)}^{\infty}\eta(\sigma)d\sigma - \int_{\zeta(\rho,0)}^{\infty}\eta(\sigma)d\sigma\right] - \frac{a}{\sqrt{t}}\eta(z(\rho,0)) - \frac{2a\sqrt{t}}{M}\eta(\zeta(\rho,0)$$

$$+ \int_0^t \frac{\rho(\sigma)\dot{\rho}(\sigma)}{\sqrt{t-\sigma}}\left\{\frac{z\eta(z)}{\sqrt{t-\sigma}} - \frac{1}{M}\left[\frac{1}{\sqrt{\pi}} - \eta(z)\right] - \frac{\zeta}{\sqrt{t-\sigma}}\eta\left(\frac{M-1}{\sqrt{t-\sigma}}\right)\right\} d\sigma ,$$

and

$$(37)\quad I[\rho] = \frac{2a\rho(t)}{M}\left[\int_{-z(\rho,0)}^{\infty}\eta(\sigma)d\sigma - \int_{\zeta(\rho,0)}^{\infty}\eta(\sigma)d\sigma\right] + \frac{a}{\sqrt{t}}\eta(\zeta(\rho,0)) + \frac{2a\sqrt{t}}{M}\eta(z(\rho,0))$$

$$- \int_0^t \frac{\rho(\sigma)\dot{\rho}(\sigma)}{\sqrt{t-\sigma}}\left\{-\frac{\zeta}{\sqrt{t-\sigma}}\left[\eta\left(\frac{M-1}{\sqrt{t-\sigma}}\right) - \eta(\zeta)\right] - \frac{1}{M}\left[\frac{1}{\sqrt{\pi}} - \eta(\zeta)\right]\right\} d\sigma\ .$$

The class C of functions $\rho$ for which D and I are "decreasing" and "increasing", respectively, is constructed in [10], where the following theorem is proved.

Theorem 5.

If $\rho_1$, $\rho_2 \in C$ for $0 \leq t \leq \bar{t}$ and if

$$\rho_1 \dot{\rho}_1 \leq \rho_2 \dot{\rho}_2$$ (1)

then

$$\rho_1 \leq \rho_2\ , \qquad \dot{\rho}_1 \leq \dot{\rho}_2$$

and

$$D[\rho_1] \geq D[\rho_2]\ , \qquad I[\rho_1] \leq I[\rho_2]$$

for $0 \leq t \leq \bar{t}$ .

The class C is composed (essentially) of all continuously differentiable positive decreasing functions $\rho(t)$ for which

---

(1) Throughout this paper, when comparing two functions $f(t)$ and $g(t)$, the statement $f \leq g$ shall mean $f(t) \leq g(t)$ for each t in the specified interval.

(38) $$z(\rho, \sigma) > -{}^{1}/_{\sqrt{2}} \quad .$$

The restriction (38) is necessary even in [5] and is practically equivalent to requiring

(39) $$\rho(t)\dot{\rho}(t) \geq -\beta\left(1 + \frac{1}{\sqrt{\pi t}}\right)$$

with

(40) $$\beta \leq \frac{1}{1+\sqrt{8/\pi}} \sim .38 \quad .$$

In attempting to set up an iteration scheme the key problem is that of determining a lower bound, that is a function $W(t) \varepsilon C$ such that

(41) $$D[1] + I[W] \geq W\dot{W} \quad .$$

Then for any $\rho_1$, $\rho_2 \varepsilon C$, if $\rho_1\dot{\rho}_1 \leq 0$ and $\rho_2\dot{\rho}_2 \geq W\dot{W}$ we would have, by Theorem 5

(42) $$D[\rho_1] + I[\rho_2] \geq D[1] + I[W] \geq W\dot{W} \quad .$$

We were not able to construct a $W(t)$ such that (41) holds for all t, and this is the cause of the time restriction discussed above. The $W(t)$ that we shall use is constructed as follows.

On assuming $0 \leq W(t) \leq 1$, we can show that

$$(43)\qquad D[1] + I[W] \geq -A(t) + \int_0^t W(\sigma)\dot{W}(\sigma)\,.\,f(t,\sigma)d\sigma$$

where the following definitions have been used.

$$(44)\qquad A(t) = \alpha\left(z\int_0^{\frac{M-1}{\sqrt{t}}} \eta(\sigma)d\sigma + \frac{1}{\sqrt{\pi t}}\right),$$

$$(45)\qquad \int_0^t \frac{1}{\sqrt{\sigma}} f(t,\sigma)d\sigma = \frac{1}{\sqrt{t}}\left[1 - B(t)\right],$$

$$(46)\qquad B(t) = 1 - \frac{2\sqrt{\pi t}}{M}\int_0^{M/\sqrt{t}} \eta(\sigma)d\sigma - M\sqrt{\pi}\left(\frac{\eta\left(\frac{M-1}{\sqrt{t}}\right)}{M-1} - \frac{\eta\left(M/\sqrt{t}\right)}{M}\right).$$

If

$$(47)\qquad \sqrt{\sigma}\, W(\sigma)\dot{W}(\sigma) \geq \sqrt{t}\, W(t)\dot{W}(t)$$

then (43) implies

$$(48)\qquad D[1] + I[W] \geq -A(t) + \sqrt{t}\, W(t)\dot{W}(t)\int_0^t \frac{1}{\sqrt{\sigma}} f(t,\sigma)d\sigma$$

or

$$(49)\qquad D[1] + I[W] \geq -A(t) + W(t)\dot{W}(t)\,(1 - B(t))\,.$$

Therefore, if we define W(t) by

$$(50)\qquad \begin{cases} W(t)\dot{W}(t) = -\dfrac{A(t)}{B(t)} \\[2ex] W(0) = 1 \,, \end{cases}$$

with A(t) and B(t) given by (44) and (46) we see immediately upon substitution in (49) that (42) is satisfied. It can also be verified that (47) is valid for this choice of W.

Unfortunately, the function B(t) has a zero, $t_B$,($t_B \sim M^2/3$) and hence $W\dot{W}$ is defined only for $0 < t < t_B$ .

We now define the sequence of functions $\{\rho_n(t)\}$ and the sequences $\{a_n\}$ and $\{k_n\}$ of numbers as follows :

$$(51)\qquad \begin{cases} \rho_o(t)\dot{\rho}_o(t) = W(t)\dot{W}(t) & 0 < t \leq a_1 \\[2ex] \rho_o(0) = 1 \end{cases}$$

$$(52)\qquad \rho_1(t) \equiv 1$$

For n = 1, 2, ...

$$(53)\qquad \begin{cases} \rho_{2n+1}(t)\dot{\rho}_{2n+1}(t) = \begin{cases} D[\rho_{2n-1}] + I[\rho_{2n-2}] & , \ 0 < t < a_{2n-1} \\ W(t)\dot{W}(t) & , \ a_{2n-1} \leq t \leq a_{2n} \end{cases} \\[3ex] \rho_{2n}(0) = 1 \end{cases}$$

$$(54)\qquad \begin{cases} \rho_{2n+1}(t)\dot{\rho}_{2n+1}(t) = \begin{cases} D[\rho_{2n}] + I[\rho_{2n-1}] & , \ 0 < t < a_{2n+1} \\ 0 & , \ a_{2n+1} \leq t \leq T \end{cases} \\[3ex] \rho_{2n+1}(0) = 1 \end{cases}$$

Here $a_1 = \min(a_1^*, T)$, where $a_1^*$ is the smallest zero of $W(t)$ and $T(< t_B)$ is defined as the unique positive solution of

$$(55) \qquad W(T)\dot{W}(T) = w(T)\dot{w}(T) \quad ;$$

$w(t)$ in (55) is defined by

$$(56) \qquad w(t)\dot{w}(t) = -\beta\left(1 + \frac{1}{\sqrt{\pi t}}\right) \quad ,$$

$$(57) \qquad \beta = \sqrt{\frac{\pi\alpha}{2+\alpha}} \quad .$$

This definition of $\beta$ is dictated by the method of proof of one of the theorems. Also, (57) places a further restriction on $\alpha$. We must have (see (40)) $\beta \leq (1 + \sqrt{8/\pi})^{-1}$, i.e.

$$(58) \qquad \alpha \leq \frac{2}{(\sqrt{\pi}+\sqrt{8})^2} \sim .095$$

For $n = 1, 2, \ldots$

$$a_{2n} = \min(a_{2n}^*, T) \quad , \quad a_{2n+1} = \min(a_{2n+1}^* , T)$$

where $a_{2n}^*$ is the smallest zero of $\rho_{2n}(t)$ and $a_{2n+1}^*$ is the smallest zero of $\rho_{2n+1}(t)\dot{\rho}_{2n+1}(t)$ .

Also

$$(59) \qquad k_o = 0 \quad , \quad k_1 = 1$$

(60) $$k_{2n} = \rho_{2n}(a_{2n-1}) \quad , \quad k_{2n+1} = \rho_{2n+1}(a_{2n+1})$$

Most of the above definitions are illustrated in the schematic drawing (Fig. 4).

We now have the following

Theorem 6.

For $\alpha$, $\beta$ satisfying (57), (58) there exists a positive number T defined by (55) such that

a) The sequence $a_n$ converges either to T or to a number $t_o < T$

b) The sequence $k_n$ converges either to zero (when $t_o < T$) or to a number $K \geq 0$ where $R(T) = K$ .

c) For any $\bar{t} < \min(t_o, T)$, there exists an N such that for $n \geq N$ each $\rho_n$ is defined in $0 \leq t \leq \bar{t}$ and the sequence $\rho_n$ converges to a function R(t) which is continuously differentiable in the range $0 < t < \min(t_o, T)$. R(t) is the unique solution of (81) and $\dot{R}(t) < 0$ .

d) For any n

$$\rho_{2n} \leq \rho_{2n+2} \leq R \leq \rho_{2n+3} \leq \rho_{2n+1}$$

$$\dot{\rho}_{2n} \leq \dot{\rho}_{2n+2} \leq \dot{R} \leq \dot{\rho}_{2n+3} \leq \dot{\rho}_{2n+1}$$

where the inequality between any two functions holds throughout their common domain of definition.

## V. Estimates for R(t) From the Iteration Method.

Theorem 6 supplies us with a sequence of bounds for R and $\dot{R}$.< However these bounds are extremely complicated in form and hence we shall now produce some more usable bounds by simplifying a few of the $\rho_n$. We have

$$(61) \qquad R(t)\dot{R}(t) \;\geq\; \rho_o(t)\dot{\rho}_o(t) \;=\; W(t)\dot{W}(t) \;=\; -\frac{A(t)}{B(t)} \quad ,$$

It is easily shown that

$$(62) \qquad A(t) \;\leq\; \alpha\left(1 + \frac{1}{\sqrt{\pi t}}\right) \quad ,$$

while

$$(63) \qquad B(t) \;\geq\; 1 - \frac{2}{M-1} - \frac{\sqrt{\pi}}{M}\sqrt{t} \;\geq\; 0 \quad .$$

These results hold if

$$(64) \qquad M \;>\; 3$$

and

$$(65) \qquad t \;<\; \frac{1}{\pi}\left(\frac{M^2-3M}{M-1}\right)^2 \;<\; t_B \quad .$$

On integrating (61) we obtain

$$\frac{1}{2}\left(W^2(t) - 1\right) \;\geq\; -\int_0^t \frac{\alpha(1+1/\sqrt{\pi\sigma}\,)}{1-\frac{2}{M-1} - \frac{\sqrt{\pi}}{M}\sqrt{\sigma}}\, d\sigma \quad ,$$

or

$$(66) \qquad R^2(t) \geq W^2(t) \geq 1 + \frac{4aM}{\sqrt{\pi}} E(t) \equiv \psi^2(t)$$

In (64) E(t) is defined by

$$(67) \qquad E(t) = \sqrt{t} + \frac{M^2-2M-1}{\sqrt{\pi}(M-1)} \log\left(1 - \frac{\sqrt{\pi}(M-1)}{M(M-3)} \sqrt{t}\right) .$$

From this we obtain

$$(68) \qquad \dot{R}(t) \geq -\frac{A(t)}{B(t)}\left(1 + \frac{4aM}{\sqrt{\pi}} E(t)\right)^{-1/2} .$$

These bounds were referred to in the Introduction.

In order to obtain upper bounds for R and $\dot{R}$ we shall estimate $\rho_3$. By definition

$$\rho_3\dot{\rho}_3 = \begin{cases} D[\rho_2] + I[\rho_1] , & 0 < t < a_3 \\ 0 , & a_3 \leq t \leq T \end{cases}$$

but, in the range $0 < t < a_3$, since $\rho_2\dot{\rho}_2 \geq w\dot{w}$ and $\rho_1 \equiv 1$, we have

$$\rho_3\dot{\rho}_3 \leq D[w] + I[1] .$$

On eliminating some of the small negative terms and making some further simplifications we obtain the following upper bound:

$$(69)\quad R\dot{R} \leq \rho_3\dot{\rho}_3 \leq P\dot{P} \equiv -\frac{1}{\sqrt{t}}\left\{a\eta\left(\frac{f(t)}{w(t)}\right) - \frac{\beta}{\sqrt{\pi}w(t)}\,\mathrm{erf}\,(\beta/\sqrt{\pi})\right\}$$

$$+\ a\left\{\frac{2\sqrt{t}}{M\sqrt{\pi}} + \frac{1}{\sqrt{t}}\,\eta\left(\frac{M-1}{\sqrt{t}}\right) + \frac{1}{M}\left[1 - \mathrm{erfc}\left(\frac{M-1}{\sqrt{t}}\right)\right]\right.$$

$$\left. -\ \left[\mathrm{erfc}\,(1/2\sqrt{t}) - \mathrm{erfc}\left(\frac{M-1}{\sqrt{t}}\right)\right]\right\}$$

$$+\ \frac{\beta}{w(t)}\left\{\frac{\beta}{2} + \mathrm{erf}(f(t))\right\}$$

where

$$(70)\qquad f(t) = \frac{\beta}{2}\left(\frac{2}{\sqrt{\pi}} + \sqrt{t}\right)$$

$$(71)\qquad w(t) = \left(1 - 4\sqrt{t}\,f(t)\right)^{1/2}$$

and

$$(72)\qquad \mathrm{erfc}(x) = 1 - \mathrm{erf}(x) = 1 - \frac{2}{\sqrt{\pi}}\int_0^x \exp(-\sigma^2)\,d\sigma$$ (1)

In order to obtain upper bounds on $R$ and $\dot{R}$ from (69) it is necessary to integrate $P\dot{P}$ numerically, to get $R^2 \leq P^2$ and then $\dot{R} \leq P\dot{P}/\sqrt{P^2}$.

---

(1) These are tabulated functions. See e.g. Pierce [9].

## VI. Estimates for R(t) from Green's Theorem.

By again applying Nirenberg's theorems (see Section II) we can establish the following theorem concerning the solution c(r, t):

Theorem 7.

a) $$0 \leq c(r, t) \leq 1$$

b) $$c_t(M, t) \geq 0 .$$

c) $$\lim_{t \to \infty} c(r, t) = c_\infty = \begin{cases} 1 & , \text{ for } 1 \leq M \leq \overline{M} \\ (\overline{M}/M)^{1/3} & , \text{ for } M > \overline{M} \end{cases}$$

where

$$\overline{M} = \left(\frac{1+\alpha}{\alpha}\right)^{1/3} . \tag{73}$$

(For $\alpha = 2 \times 10^{-5}$, $\overline{M} = 36.84$). Physically, part a) states that the vapor density remains between the initial density and the saturation density. Part b) states that the vapor density at the container wall increases with time as the drop evaporates. Part c) gives the exact final value of the density for both incomplete and complete evaporation. Theorem 7 holds wherever the solution c(r, t) exists for all $t > 0$ .

We shall now establish a number of bounds for R(t) and for the evaporation time, $t_o$, (where it exists). The bounds are contained in Theorem 8 which is stated in the Introduction.

Proof of Theorem 8.

We apply a special case of Green's Theorem, (see e.g. [1]): for any regular solution u(r, t) of the equation $u_{rr} = u_t$ in a

closed domain D we have, for any constants a and b,

$$(74)\qquad \oint \left\{ [ar + b]u\, dr + [(ar + b)\, u_r - au]dt \right\} = 0 .$$

On substituting the data of our problem into formula (74) we obtain, (after simplifying and stating in terms of c(r, t)

$$(75)\qquad \frac{\alpha+1}{\alpha}\left\{\frac{a}{3}[1 - R^3(t)] + \frac{b}{2}[1 - R^2(t)]\right\}$$

$$= bt - b\int_0^t c(M, \tau)d\tau + \int_{R(t)}^M (ar + b).r.c(r, t)dr .$$

All parts of Theorem 8 now follow from (75) by choosing appropriate values for a and b and applying Theorem 7. For example, let a = 0, b = 1 in (75) to get

$$(76)\quad \frac{\alpha+1}{2\alpha}[1 - R^2(t)] = t - \int_0^t c(M,\tau)d\tau + \int_{R(t)}^M rc(r, t)dr .$$

Since $c(M, \tau) \leq c_\infty$ , $c \geq 0$ , we can write

$$(77)\qquad \frac{\alpha+1}{2\alpha}[1 - R^2(t)] \geq t - c_\infty t .$$

From (77) part a) follows. Parts b), c), d) are proved by similar arguments. Parts e) and f) are proved by setting $R(t_o) = 0$ in (75) and then applying the estimate s.

By using bound f) it can be shown that for $M \geq 275$, $T \geq t_o$ so that in this case the iteration procedure of Section IV gives the complete solution.

It should be noted here that although the method of this section produces some good bounds for $R(t)$ and $t_0$ it gives no information whatever on the rate of evaporation $\dot{R}(t)$. Thus the results of Section V supply the only bounds on $\dot{R}(t)$.

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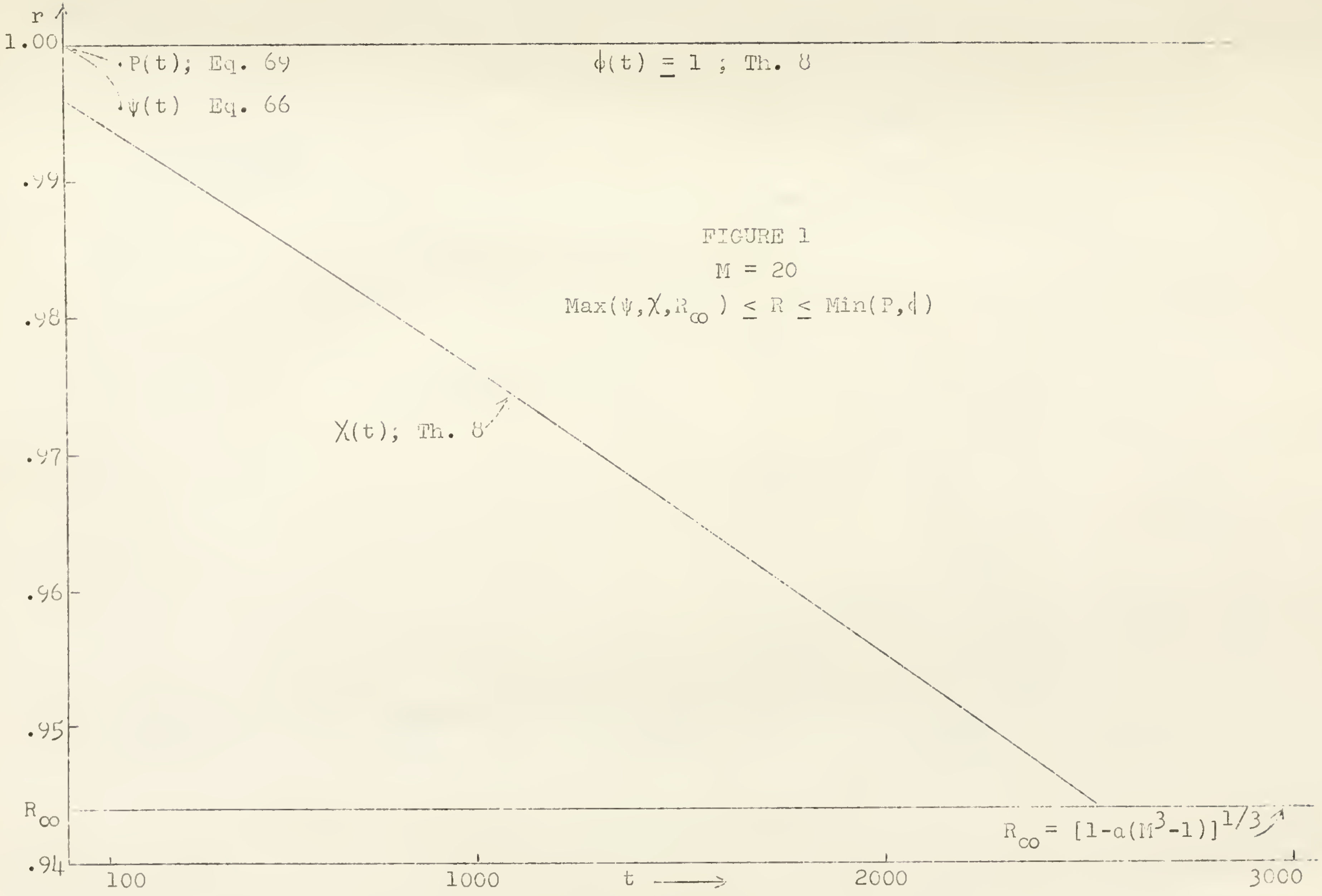


FIGURE 1

$M = 20$

$\mathrm{Max}(\psi, \chi, R_\infty) \leq R \leq \mathrm{Min}(P, \phi)$

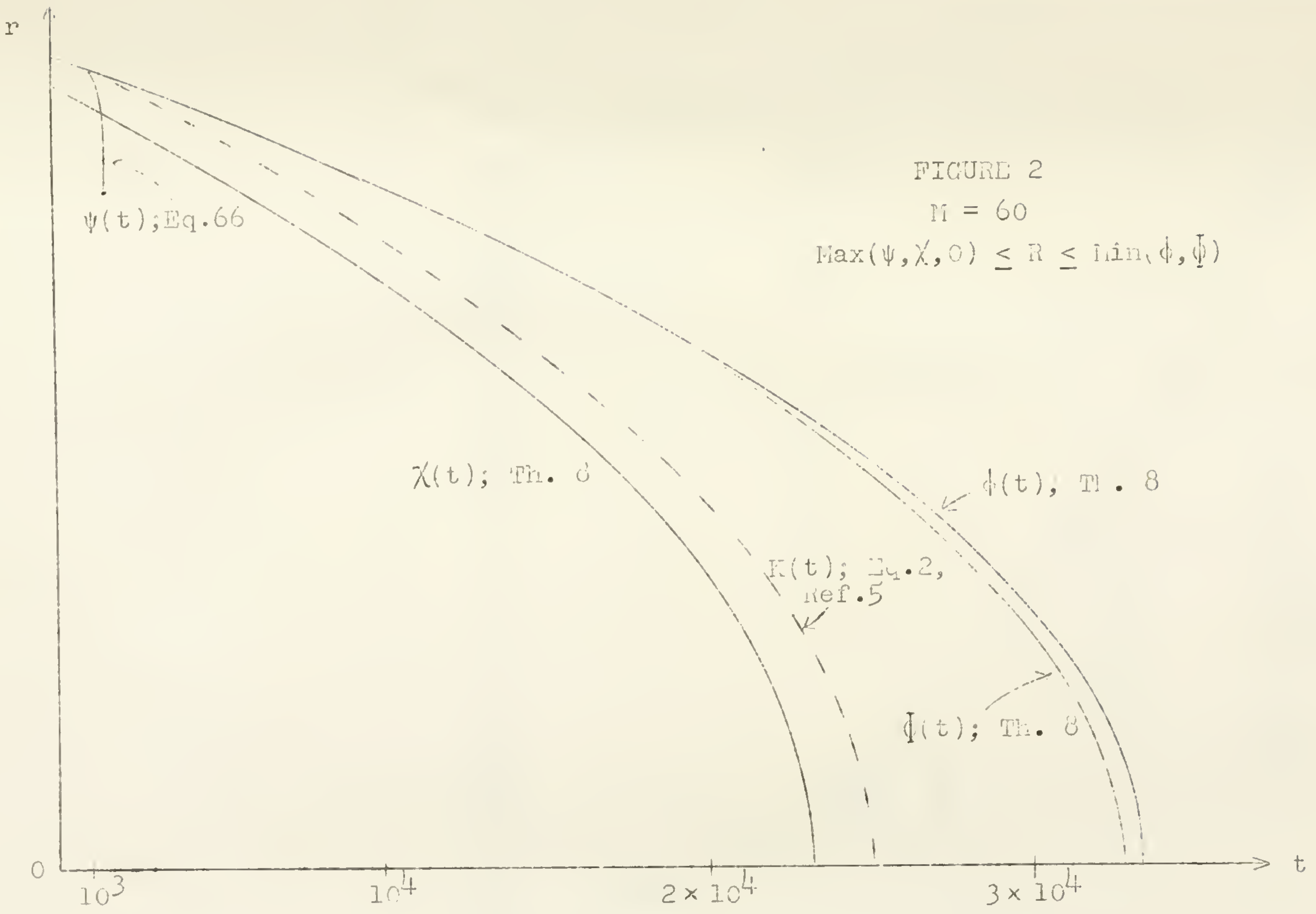


FIGURE 2

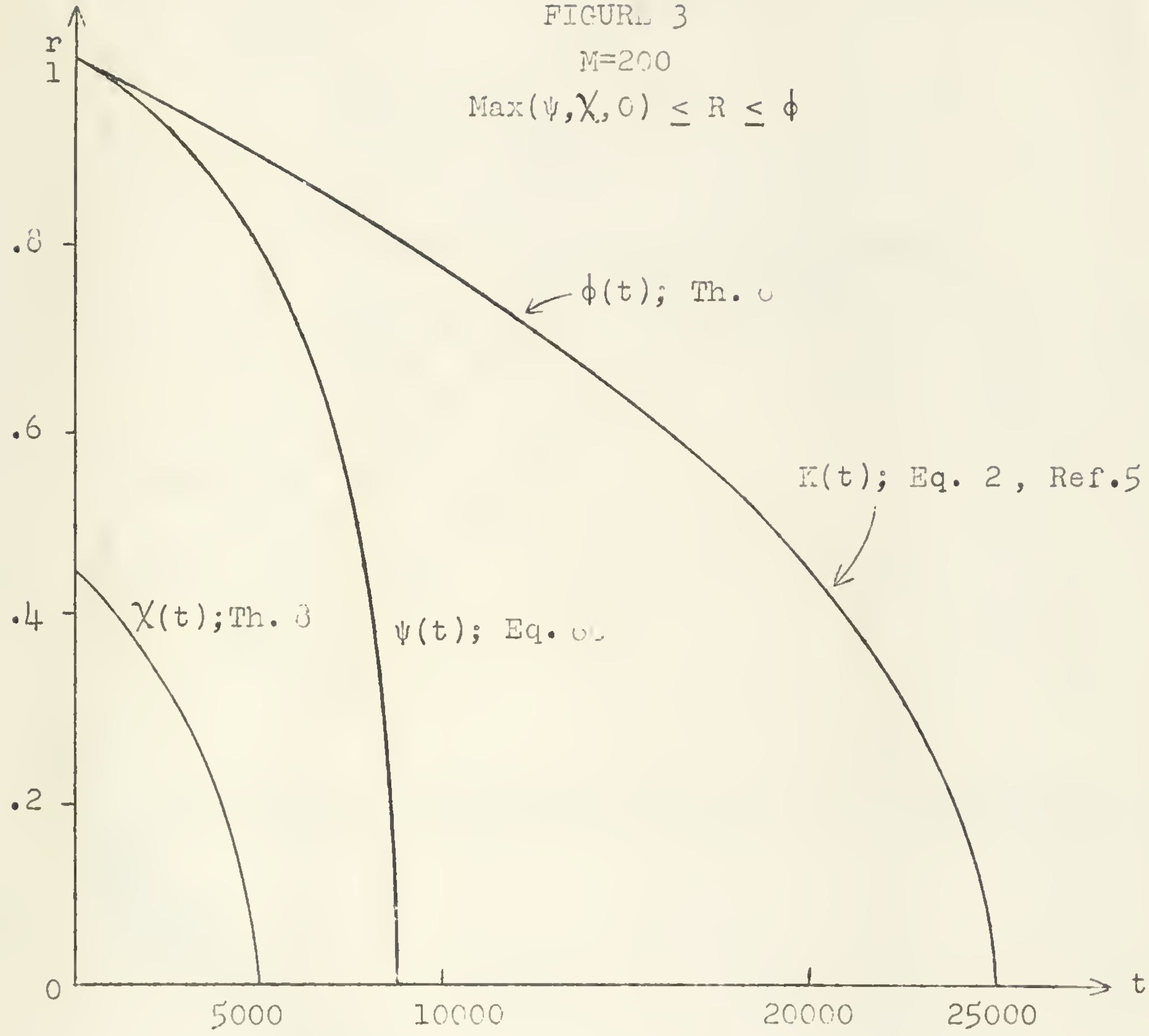
M = 60

$\mathrm{Max}(\psi, \chi, 0) \le R \le \mathrm{Min}(\phi, \Phi)$

FIGURE 3

M=200

$\mathrm{Max}(\psi,\chi,0) \leq R \leq \phi$



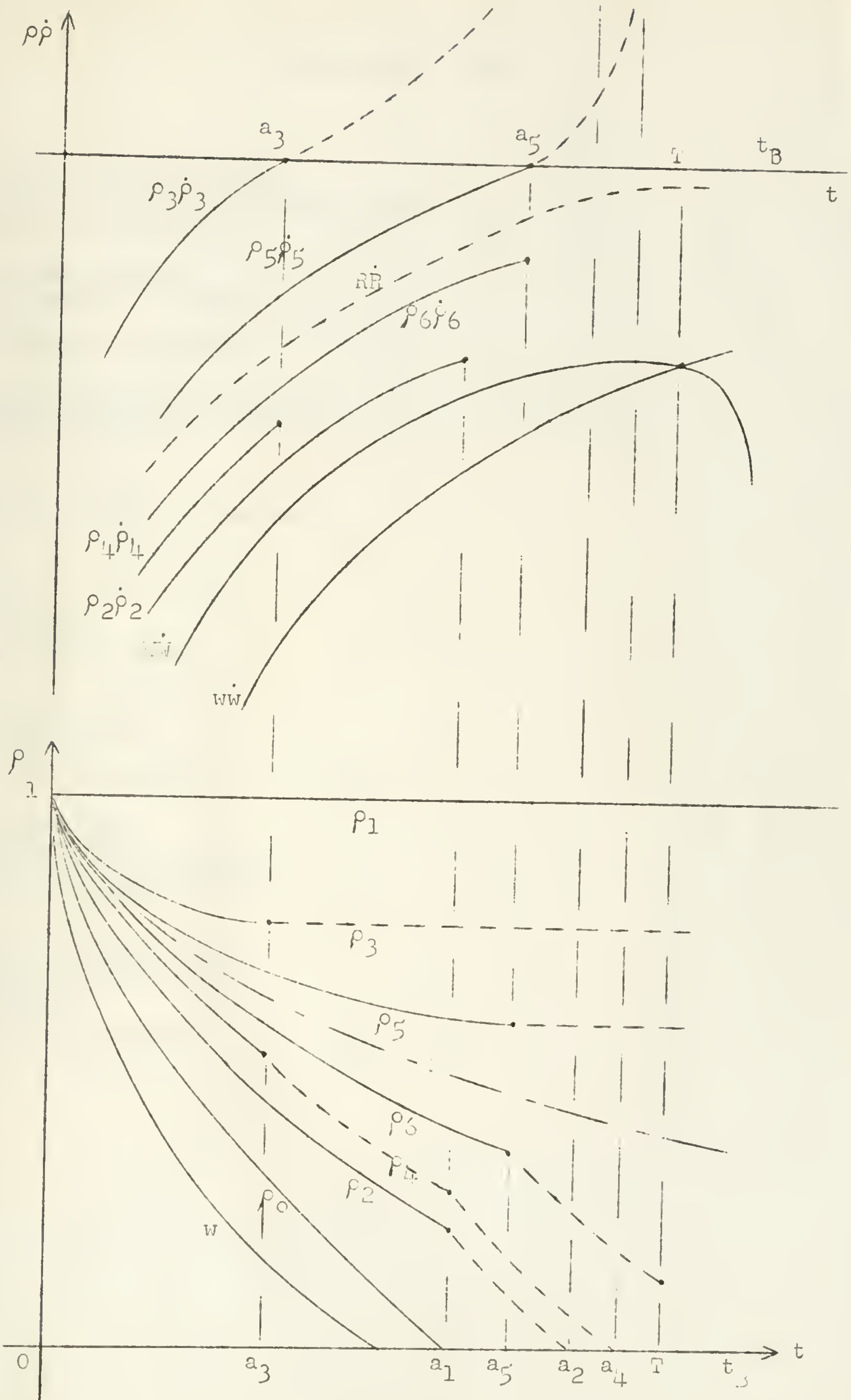

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FIGURE 4

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